Hydride formation thermodynamics and hysteresis in individual Pd nanocrystals with different size and shape

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Abstract

Physicochemical properties of nanoparticles may depend on their size and shape and are traditionally assessed in ensemble-level experiments, which accordingly may be plagued by averaging effects. These effects can be eliminated in single-nanoparticle experiments. Using plasmonic nanospectroscopy, we present a comprehensive study of hydride formation thermodynamics in individual Pd nanocrystals of different size and shape, and find corresponding enthalpies and entropies to be nearly size- and shape-independent. The hysteresis observed is significantly wider than in bulk, with details depending on the specifics of individual nanoparticles. Generally, the absorption branch of the hysteresis loop is size-dependent in the sub-30 nm regime, whereas desorption is size- and shape-independent. The former is consistent with a coherent phase transition during hydride formation, influenced kinetically by the specifics of nucleation, whereas the latter implies that hydride decomposition either occurs incoherently or via different kinetic pathways.

Main

Palladium (Pd) constitutes the most important model system for fundamental studies of metal–hydrogen interaction, which is central in areas such as hydrogen storage[1], heat storage[2], metal hydride batteries[3], hydrogen sensors[4], smart

windows[5] and switchable mirrors[6]. Hydrogen forms a stable hydride with Pd, basically without activation barriers[7]. During absorption, H_2 dissociates on the Pd surface and subsequently occupies surface, subsurface and interstitial lattice sites according to their specific energetics[8]. In the bulk, at low hydrogen partial pressures, the hydrogen atoms form a solid solution (α-phase). At each temperature below the critical temperature, there is a pressure at which the chemical potentials of hydrogen in the gas phase, α-phase and hydride (β-phase) are equal, and the first-order transition to the β-phase is initiated and manifested as a 'plateau' in a pressure–composition (p–C) isotherm. In addition, hysteresis occurs between hydride formation and decomposition, induced by the appearance of a macroscopic energy barrier for the transformation between the two phases due to lattice strain[9] imposed by an increase of the lattice parameter of about 3.5% in the hydride[7]. At the same time, a change of the complex permittivity of Pd takes place[10].

In the related fields it is essential to gain deeper understanding of the role of nanosizing because nanomaterial engineering provides a powerful means to optimize material performance[11,12]. A summary of the corresponding findings for traditionally studied ensembles of Pd nanoparticles includes: lowering of the critical temperature for separation of the α- and β-phases with decreasing particle size[13], narrowing of the two-phase region[14], decreasing absorption–desorption hysteresis and increasing slope of the plateau of the corresponding loop[15,16,17,18], and apparent compensation for the influence of surface tension by absorption at subsurface sites[19]. The influence of the particle size/shape distribution on these findings is, however, not fully clear[20]. Other frequent complicating factors are different types of surfactants, polymeric stabilizers or strong interactions with the support/host matrix that may affect lattice strain and its relaxation during hydrogenation[21].

With the development of nanoplasmonic sensing, it recently became possible to advance from studies of confinement effects in Pd thin films and arrays/ensembles of Pd nanoparticles to the investigation of hydrogen sorption at the single-nanoparticle level, eliminating ensemble-averaging artefacts[4,22,23,24,25]. However, these initial single-particle studies did not provide deeper insight into the corresponding physics. The first detailed single-particle experiments were performed by Baldi *et al.* with individual Pd nanocubes at low pressure and temperature by means of electron energy loss spectroscopy[26]. Instead of a slope in the plateau region observed earlier at the ensemble level for Pd nanocubes by Bardhan *et al.*[27], they found a sharp phase transition and a size-dependent absorption plateau pressure (the thermodynamics was not quantified). This was explained by a model assuming phase coherence and tensile strain in the particle core, induced by a thin 1 nm subsurface hydride layer, which mediates the phase transition[26]. In contrast, the treatment by Bardhan *et al.* invoked a thermal-fluctuation-mediated phase transition to explain the observed size-dependent thermodynamic parameters[27].

Herein, we apply non-invasive single-particle plasmonic nanospectroscopy for the first comprehensive experimental assessment of both hydrogenation thermodynamics and hysteresis in individual, surfactant-free, Pd nanocrystals over an unprecedented size (from 17 nm to over 100 nm) and shape range (single-crystalline nanocubes, nanooctahedra and twinned nanorods), to address the above contradictory findings in detail. We rely on wet-chemically synthesized Pd–Au heterodimers, created by electrostatic self-assembly of plasmonic Au nanoantennas and shape-selected Pd nanocrystals we have introduced earlier[28] (see also Methods). Hydrogen sorption is tracked by measuring the spectral shifts of the plasmonic scattering peak of individual dimers, which is proportional to the hydrogen concentration in a Pd particle[29,30], as here also confirmed specifically by finite-difference time-domain (FDTD) simulations for the three investigated Pd nanoparticle shapes.

Single-particle plasmonic nanospectroscopy

At nanoscopic length scales, metallic nanoparticles exhibit localized surface plasmon resonance (LSPR; ref. 31). We rely on the fact that the LSPR spectral position of a Au nanoantenna placed adjacent to a Pd nanoparticle is sensitive to the changes in permittivity and volume expansion induced in Pd on hydrogen sorption (Fig. 1)[32]. At the same time the plasmonic antenna serves as a strong light scattering unit, which makes it 'visible' in a dark-field optical microscope. This is important because small Pd nanoparticles (as well as many other metals) on their own have poor light scattering properties due to strong absorption[33]. Thus, the Au nanoantenna acts both as a local nanoprobe for the hydrogen sorption in the adjacent Pd particle, and as an efficient signal transducer for dark-field scattering spectroscopy (DFSS).

Figure 1: Heterodimer arrangement of a plasmonic Au nanoantenna combined with a shape-selected Pd nanoparticle.

a, Artist's view: As H_2 molecules (red) dissociate and are absorbed into the Pd cube, the process can be detected by the plasmonic Au particle (sphere) through a spectral shift of its LSPR readout at the single-particle level due to its large scattering cross-section at visible frequencies. **b**, Side-view scanning electron microscopy (SEM) image of a Au–Pd nanocube arrangement. **c**, Representative transmission electron microscopy (TEM) image at high magnification. **d**,**e**, Top-view SEM images of Au–Pd octahedron and Au–Pd nanorod dimers, respectively. The scale bars are 100 nm (**b**,**d**,**e**) and 10 nm (**c**).

Figure 2a, b shows two characteristic scattering spectra recorded from two representative Au–Pd nanocube heterodimers, before and after transition from the metallic to the hydride phase. A clear shift of the scattering peak to shorter wavelengths is observed. Figure 2c, dillustrates the time-resolved hydrogen absorption traces measured at 333 K for the same two Au–Pd-cube heterodimers. The hydrogen partial pressure was increased in steps, and for each step the dwell time was chosen such that the particle reached the new equilibrium state for the corresponding pressure, as determined by the fact that the peak position had stabilized. With increasing pressure, a continuous spectral blue shift is observed in the $\Delta\lambda_{max}$ signal (for a negative control see Supplementary Fig. 1). This corresponds to continuous absorption of hydrogen into the dilute α-phase up to the more sudden 'jump' in the signal, which corresponds to the first-order transition of the α-phase into the hydride. To corroborate our approach, we performed FDTD simulations of the light scattering by various Au–Pd nanodimers (Fig. 2e, f and Supplementary Figs 27 and 28). The general trend of the experimentally observed blue shift on hydrogen sorption is reproduced very well, thus validating our data interpretation.

Figure 2: Experimental procedure and theoretical FDTD simulations.

a,**b**, Representative scattering spectra of individual Au–Pd heterodimers: blue (red) dots correspond to the raw scattering data before (after) hydride formation, as measured for Pd cubes with sizes 45 nm and 18 nm, respectively. The shift in the LSPR wavelength, $\Delta\lambda_{max}$, is read out by fitting a Lorentzian curve (solid lines) to the raw scattering data. The insets show SEM images of the heterodimers (scale bars, 100 nm). **c**,**d**, Corresponding time evolution of $\Delta\lambda_{max}$ during the hydrogen sorption and phase transition from metal to hydride for the particles shown in **a**,**b**. **e**, FDTD simulation scheme of a single Au nanosphere with radius 50 nm and an attached Pd nanocube of 20 nm edge length, which sits on 50 nm SiO_2 on top of the Si substrate to mimic the experimental conditions. Incident light is linearly polarized and introduced via total-field/scattered-field conditions (inner red box). Scattering is measured as the flux of the Poynting vector through the surface of the outer black box. **f**, Results of the simulation shown as scattering cross-sections for the Au/PdH_x heterodimer with the Pd cube in the metallic (no hydrogen, solid blue) or the fully hydrided state (black dash-dotted), and with hydrogen-induced changes of only the lattice constant (volume increase, dashed red) or only the permittivity (volume constant, dotted green) deconvoluted for an initial nanocube edge length of 20 nm (detailed discussion in the Supplementary Information).

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Hydride formation thermodynamics

Tracking the $\Delta\lambda_{max}$ signal with increasing hydrogen uptake makes it possible to record pressure (p)–$\Delta\lambda_{max}$ isotherms of hydrogen sorption in individual Pd nanocubes, which can be directly interpreted as conventional p–C isotherms[29,30] (Fig. 3a–l), including the α-phase at low hydrogen pressures, β-phase at high pressures, and the phase transition region manifested as a sharp plateau. Moreover, we observe distinct and exceptionally wide hysteresis between absorption and desorption for all sizes (Supplementary Fig. 2). The enthalpy (ΔH) and entropy (ΔS) changes per hydrogen molecule on hydride formation in individual nanocubes can now be calculated via the temperature (T) dependence of the plateau pressure (p) using the Van't Hoff relation[34] $\ln(p/p_0) = \Delta H/(RT) - \Delta S/R$, where p_0 = 1,013 mbar—that is, from the slope in the dependence of $\ln(p/p_0)$ on $1/T$ (Fig. 4a–l). The obtained values (Fig. 4m) indicate that on average ΔH = −33 kJ $(\text{mol } H_2)^{-1}$ and ΔS = −82 J $K^{-1}(\text{mol } H_2)^{-1}$ for the nanocubes.

Figure 3: p–$\Delta\lambda_{max}$ isotherms measured at four temperatures for Pd nanocubes.

Isotherms for Pd nanocubes of decreasing size: 63 nm (**a**), 60 nm (**b**), 54 nm (**c**), 45 nm (**d**), 43 nm (**e**), 42 nm (**f**), 40 nm (**g**), 32 nm (**h**), 30 nm (**i**), 30 nm (**j**), 24 nm (**k**) and 18 nm (**l**). The measurement temperatures are 333 K (red), 323 K (green), 313 K (cyan) and 303 K (blue). The SEM images (with the scale bar of 100 nm) correspond directly to the particle from which the respective isotherms in each panel were measured. The raw data for each isotherm measurement can be found in Supplementary Figs 5–16. We also note that the origin of the narrowing of the plateau width for some low-temperature isotherms is an experimental artefact related to the long measurement times and consequent random particle movement or slight change of focus in the microscope, which slightly changes the excited plasmonic modes, and thus the sensitivity. The reproducibility of our measurements is illustrated in Supplementary Fig. 4.

Figure 4: Van't Hoff analysis.

a–l, Van't Hoff plots constructed from the corresponding absorption isotherm data depicted in Fig. 3. **m**, Table summarizing enthalpies and entropies of hydride formation in Pd nanocubes of different sizes as obtained from the Van't Hoff plots in **a–l**. The uncertainty range for ΔH and ΔS given in the upper row of each cell results from the maximum possible range in the plateau pressure values and the consequent maximal variation in ΔH and ΔS(see Supplementary Information and Supplementary Fig. 24 for details). The uncertainty range for ΔH and ΔS given in the bottom row of each cell results from the uncertainty in the linear regression in the Van't Hoff plots used to derive the minimal, mean and maximal $\Delta H$and ΔS, respectively.

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As the next step, we turn to p–$\Delta\lambda_{max}$ isotherms and corresponding Van't Hoff plots for Pd octahedra (with (111) facets as opposed to (100) for nanocubes[35]) and Pd nanorods (with (100) surfaces as in cubes but 5-fold twinned[35]; see Supplementary Fig. 33), as shown in Fig. 5. These measurements yield on average $\Delta H = -36$ kJ (mol H_2)$^{-1}$ and $\Delta S = -89$ J K^{-1} (mol H_2)$^{-1}$ for the rods, and $\Delta H = -32$ kJ (mol H_2)$^{-1}$ and $\Delta S = -75$ J K^{-1} (mol H_2)$^{-1}$ for the octahedra. These values are within the range of values reported for Pd bulk ($\Delta H = -37$ kJ (mol H_2)$^{-1}$, $\Delta S = -92.5$ J K^{-1} (mol H_2)$^{-1}$; ref. 36) and thin films ($\Delta H = -34$ kJ (mol H_2)$^{-1}$, $\Delta S = -82.4$ J K^{-1} (mol H_2)$^{-1}$; ref. 37).

Figure 5: p-$\Delta\lambda_{max}$ isotherms measured at four temperatures for Pd nanoparticles of different shape.

a–c, Isotherms for octahedra with an approximate diameter of circumscribed sphere ~85 nm. Insets are SEM images of the nanoparticles. **d–f**, Isotherms for rods with approximate dimensions for width and length ~38 × 137 nm (**d**), 38 × 215 nm (**e**) and ~47 × 185 nm (**f**). Insets are SEM images of the nanoparticles. In **a–f** the measurement temperatures are 333 K (red), 323 K (green), 313 K (cyan) and 303 K (blue) and the scale bars in the SEM images is 100 nm. **g–l**, Van't Hoff plots constructed from the corresponding isotherm data depicted in **a–f**. **m**, Table summarizing enthalpies and entropies of hydride formation in Pd nanoparticles of different shapes as obtained from the Van't Hoff plots in **g–l**. The uncertainty range for ΔH and ΔS given in the upper row of each cell results from the maximum possible range in the plateau pressure values and the consequent maximal variation in ΔH and ΔS (see Supplementary Information and Supplementary Fig. 24 for details). The corresponding range given in the bottom row results from the uncertainty in the linear regression in the Van't Hoff plots used to derive the minimal, mean and maximal ΔH and ΔS, respectively. The raw data for each isotherm measurement can be found in Supplementary Figs 17–22.

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To put these numbers into perspective, it is important to discuss their accuracy. In principle, there are two major sources of uncertainty in the quantification of ΔH and ΔS. The first source of uncertainty is accurate determination of the true plateau pressure, which is particularly accentuated in the case of sloping plateaux. To take this into account, we apply the procedure described in detail in the Supplementary Information. The second source of uncertainty relates to the linear regression in the Van't Hoff analysis and the quality of the fit[19]. The estimated uncertainties in ΔH and ΔS related to these two contributions are significant (see the tables in

Figs 4 and 5) and thus crucial for our (and other similar studies) interpretation of ΔH and ΔS.

With this information at hand we can now analyse our data specifically as a function of particle size and shape. Figure 6a, b shows a summary of all ΔH and ΔS values, respectively, for all nanocubes, octahedra and nanorods. Clearly, within the experimental accuracy, we do not observe any statistically significant dependence of the derived ΔH and ΔS values on Pd nanoparticle size or shape, although there is indication of a weak tendency of increasing $|\Delta H|$ with increasing nanocube size. Interestingly, there is also a correlation between ΔH and ΔS(Supplementary Fig. 26). This is indicative of an enthalpy–entropy compensation effect, for which we find a compensation temperature $T_{comp} = 289 \pm 14$ K from the slope of our correlation plot (Supplementary Fig. 26). Thus, as T_{comp} is in the range of the temperatures used in our experiments, the observed correlation seems to be a consequence of the limited temperature range of the experiments[38].

Figure 6: Summary of the size and shape dependence of hydride formation thermodynamics and hysteresis.

The Pd nanocube size, including the points for the octahedra and the nanorods, is plotted versus the enthalpy of hydride formation, ΔH (**a**), the entropy of hydride formation, ΔS (**b**), the plateau pressure at absorption p_{abs} (upward pointing triangles) and desorption p_{des}(downward pointing triangles) measured at 333 K (**c**), and the hysteresis width factor $\ln(p_{abs}/p_{des})$ at 333 K (**d**). The lines in **d** indicate the literature values for polycrystalline bulk Pd (10 μm foil)[36] (dashed line), a 30 nm polycrystalline Pd film[19] (dash-dotted line) and for an ensemble of polycrystalline Pd nanodisks of 300 nm in diameter and 60 nm in height[39](dotted line). Interestingly, the desorption plateau pressures are very similar for all systems, which indicates that the difference in hysteresis width is dictated entirely by the absorption plateau pressure. We also note that, according to the isotherm measurements for solubility of deuterium in single-crystalline bulk Pd (110) at 353 K (ref. 47), the factor characterizing the hysteresis width is very similar to the polycrystalline bulk at 0.47. The error bars in **a**,**b**stem from the maximum possible range in the plateau pressure values and the consequent maximal variation in ΔH and ΔS (see Supplementary Information and Supplementary Fig. 24for details). Furthermore, we notice that the uncertainty in ΔH and ΔS resulting from the error in the linear fit of the Van't Hoff plot is not included in the error bars shown, for consistency with the data in the panels below. The error bars in **c**,**d** represent the difference in pressure between the low and high pressure end of the plateau at the phase transition in the single-particle experiments. Note that they are of the same order as the symbols or smaller (in **c**), indicating very flat plateaux. The bold triangles and crosses in **c** and **d**represent the corresponding values for the particles shown in Figs 3 and 5. Light triangles

and crosses in **c** and **d** represent the data from isotherm measurements performed only at 333 K on additional Pd particles (cubes and rods) for better statistics. The shaded area in **c**indicates the slope of the absorption and desorption plateau pressures measured on ensembles of Pd nanocubes with average sizes of 23, 34 and 66 nm (Supplementary Fig. 25). Note that the single-particle data points fit very well within this range, indicating that it is the dispersion in plateau pressure between individual nanoparticles that gives rise to the slope in the ensemble experiment. The dashed line in **c** corresponds to a calculation of p_{abs}based on the subsurface hydride layer model introduced by Baldi *et al.*[26], assuming a subsurface hydride layer thickness of 0.3 nm and the corresponding hydrogen concentration of 0.44 (see Supplementary Information for details).

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Hysteresis

We now continue our analysis by comparing the equilibrium pressures for hydride formation, p_{abs}, and decomposition, p_{des}, which we for the first time are able to assess reliably both for absorption and desorption at the single-particle level. The corresponding values (Fig. 6c) measured at 333 K for all considered nanocube sizes, together with those for octahedra and nanorods, were obtained from the isotherms shown in Supplementary Figs 2 and 3. Focusing on nanocubes, we note that p_{abs}decreases with the cube size (in agreement with Baldi *et al.*[26]—however, here, studied over a much larger size range) and that the p_{abs} data points exhibit much larger dispersion than p_{des}. Moreover, p_{des} is found to be independent of both nanoparticle size and shape, indicating that the phase transition is asymmetric in the sense that potential size/shape effects manifest themselves only during absorption. In addition, the trends in dispersion between individual particles are consistent at all measured absorption temperatures (Supplementary Fig. 23), which clearly indicates that the observed effects are related to the specifics of the individual nanoparticles and not artefacts. Finally, owing to the discovery of the size and shape independence of p_{des}, which is in very good agreement with bulk values, we also conclude that the decomposition enthalpy for our particles is bulk-like and not size/shape-dependent.

The features above become even clearer following a direct comparison with p_{abs} and p_{des} determined for ensembles of Pd nanocubes with different mean size. The shaded areas in Fig. 6c indicate the corresponding extrapolated lower and upper boundaries of the plateau pressures derived from the ensemble experiments (Supplementary Fig. 25). The single-particle data fall very well within these boundaries for both p_{abs} and p_{des}. This analysis thus shows that the typical slope of equilibrium plateaux of nanoparticle systems assessed at the ensemble level is a direct consequence of the contribution of the individual particles in the ensemble. However, this is not only due to the inherent distribution of particle sizes but also,

as apparent for the first time from our single-particle data, due to the spread in plateau pressure for individual nanoparticles with nominally identical sizes.

As the last step of the analysis we now plot (Fig. 6d) the ratio between absorption and desorption plateau pressures, $\ln(p_{abs}/p_{des})$, together with corresponding values for polycrystalline Pd nanodisks[39], a 30 nm thick polycrystalline Pd film[19] and a 10 μm polycrystalline Pd foil[36]. It becomes clear that generally, for all particles (that is, independent of size/shape), the hysteresis is significantly wider. There are, however, also noticeable differences between different particle types. For instance, the hysteresis for the Pd nanorods is somewhat narrower than for the nanocubes. The same holds for two out of three octahedra, which all basically have the same size (about 85 nm diagonal). Also, for the single-crystalline Pd cubes, the trend of decreasing hysteresis width for decreasing cube size (in qualitative agreement with Baldi *et al.*[26]) now becomes even more apparent.

To understand our observations we first notice that the temperature dependence of the H_2 pressure, p_*, corresponding to the true equistability of the α- and β-phases is determined by thermodynamics. Van't Hoff plots are, however, constructed by using p_{abs}, which does not coincide with p_* owing to hysteresis, and thus depends on the details of the kinetics of nucleation and growth of the new phase. However, the difference between p_{abs} and p_* is minor compared to the dependence of these parameters on varying temperature. Therefore, Van't Hoff plots still yield reasonably accurate values of ΔH and ΔS. In contrast, the main thermodynamic factor, ΔH, is not included in the ratio p_{abs}/p_{des}, which describes hysteresis, and accordingly hysteresis is more sensitive to the kinetic parameters that govern the phase transition. The key general factors to consider in this context are H-induced lattice (coherency) strain, surface tension, subsurface hydrogen, and lattice defects/dislocations[40]. The fact that the observed values of ΔH and $\Delta S$are nearly independent of particle size and shape is in line with what one physically expects, as surface tension, which is known to affect $\Delta H$and ΔS in small nanoparticles[11], is expected to be nearly negligible for particles in our size range, above 10 nm (ref. 19; see also Supplementary Information).

The starting point for discussion of our observations related to hysteresis is that for an ideal macroscopic Pd system the H-induced strain results in the appearance of a macroscopic (proportional to the sample volume) energy barrier for a coherent transformation between the two phases[9,41]. The strain, according to Schwarz and Khachaturyan, results in a hysteresis with width $\ln(p_{abs}/p_{des}) \simeq 2.6$ for an ideal macroscopic Pd system (see Supplementary Information)[9]. For nanostructures, however, our theoretical analysis[18] and available experimental results show that this value can be appreciably lower and size-dependent in sub-10 nm Pd particles[14,16,18,42]. Focusing on hydrogen absorption, Baldi *et al.*[26] suggest that the corresponding lattice strain caused by a 1 nm subsurface hydride shell, which forms a coherent interface with the nanoparticle core in the α-phase, is significant and gives rise to size-dependent hysteresis even in nanocrystals in the tens of

nanometres size range. Applying the same formalism (see Supplementary Information for details), but assuming a thickness of the subsurface hydride layer of 0.3 nm (in agreement with our analysis of small Pd nanoparticles[19] as well as studies on single crystals[43,44]) and a hydrogen concentration of 0.44 in the subsurface layer[16], we get almost perfect agreement with our experimental data (Fig. 6c).

In view of this, it is interesting to note that the maximal absolute hysteresis width, $\ln(p_{abs}/p_{des})$, we observe for the 63 nm Pd nanocube is about 1.4 (Fig. 6d), which is appreciably lower than the value of 2.6 expected for the ideal macroscopic Pd system in the Schwarz and Khachaturyan framework[9] (see Supplementary Information). This may indicate that the H-induced coherency strain is partly relaxed already at the initial stage of the phase transition, at least beyond a certain particle size. This might happen owing to formation of dislocations, once this becomes energetically allowed. Our experiments, supported by calculations, indicate that this happens for nanocubes larger than about 30 nm (see Supplementary Information for details), where we observe a levelling-off of the hysteresis size dependence. In this picture it also becomes clear why the nanorods exhibit substantially smaller hysteresis, as plastic deformation via dislocations at their twin boundaries reduces lattice strain. Consequently, it also explains the observed spread in absorption plateau pressure found for individual nanocrystals of nominally the same size, as it implies that it is the single-particle-specific balance between the energy required to form/move a dislocation and the coherency strain energy that determines its absorption plateau pressure. This, in turn, relates to the specifics of lattice defects in the nanocrystal and highlights the importance of single-particle experiments to unearth and understand such effects.

Our final remark is related to the observed size and shape independence of p_{des}. It implies that either the hydride decomposition occurs via incoherent coexistence of the α- and β-phases (as shown for bulk Pd; ref. 45) or indicates a different interplay in the steps controlling these branches of the kinetics[46].

Conclusions

Plasmonic nanospectroscopy is effective for probing individual functional nanoparticles *in situ* (including kinetics—see Supplementary Fig. 34) and in eliminating ensemble averaging to unearth single-particle-specific effects. Here, we have employed this approach to investigate in detail the thermodynamics of the hydride formation, and to analyse the hysteresis in the metal-to-hydride phase transition in individual Pd nanocrystals with different sizes and shapes. We find that hydride formation enthalpy and entropy in the considered size range are nearly independent of particle size or shape. This result is in agreement with the general understanding that particle sizes below 10 nm are required to significantly reduce ΔH (ref. 12). We also observe a sharp hydride phase transition with flat plateaux

and with hysteresis (much) wider than for single- and polycrystalline bulk Pd, thin-film and polycrystalline nanoparticle systems. Moreover, we find an asymmetric size dependence of the hysteresis through decreasing absorption plateau pressures for decreasing particle size (in agreement with Baldi *et al.*[26]). At the same time, we find that desorption plateau pressures are constant for all investigated particle sizes and shapes, and in excellent agreement with bulk Pd data. We explain these findings within the established picture of a first-order phase transition, and the energetic interplay between dislocation formation and coherency strain at the metal–hydride interface during hydride formation. Finally, direct comparison between ensemble and single-particle measurements clearly reveals for the first time that the typical slope on equilibrium plateaux observed for nanoparticle ensembles is not only due to inhomogeneous particle size (as commonly put forward), but also a direct consequence of the specific defect structure of the individual particles—that is, the availability of dislocations to accommodate lattice strain. The latter becomes clear from the fact that nanocrystals with nominally identical size can exhibit hysteresis with widely varying width.

Methods

Au–Pd heterodimer synthesis.

The Pd nanocubes were prepared by means of a wet-chemistry colloidal synthesis method reported earlier[35]. The spherical Au nanoparticles were purchased from Sigma-Aldrich and used as received. The Au–Pd-cube/rod/octahedron heterodimers were then formed through a self-assembly process induced by a finely tuned electrostatic interaction between the Au antenna element and the Pd nanoparticle, as described in detail in the recent work by Gschneidtner and colleagues[28]. The nanorods and nanooctahedra were ‘by-products’ of the nanocube synthesis and thus formed under exactly the same conditions (but at extremely low amounts in the case of the octahedra, as the nanocube synthesis suppresses the growth of (111) facets).

Sample preparation.

The aqueous solution with heterodimer particles was dispersed onto a piece of thermally oxidized (oxide thickness 50 nm) silicon wafer. After an incubation time of 1 min the wafer was dried with nitrogen flow to remove the liquid. Before the hydrogen sorption measurements (and after scanning electron microscopy (SEM) imaging) the sample was cleaned for 1 min in hydrogen plasma (100 W, 250 mtorr, Plasma Therm Batchtop RIE 95 m) to remove the surfactants from the synthesis and to provide clean metallic Pd surfaces. X-ray photoelectron spectroscopy (XPS) analysis of the Pd cubes shows that the surfactants are removed after H_2 plasma cleaning (Supplementary Fig. 31). Transmission electron microscopy (TEM) characterization also confirmed that the Pd cubes retain their shape after the cleaning procedure (Supplementary Fig. 32).

Single-particle dark-field scattering spectroscopy.

For the sorption experiments the samples were placed in a temperature-controlled and gas-tight microscope stage (Linkam, THMS600), which was connected to a set of mass flow controllers (Bronkhorst, Low-ΔP-flow and EL-flow) to supply the desired gas flow and concentration to the sample. We used Ar as carrier gas (6.0 purity) and 25% H_2 gas in Ar (Ar 6.0 and H_2 6.0 purity) as reactants and operated the system at atmospheric pressure. The scattering signal from individual heterodimers was collected with an optical fibre (Ocean Optics, ultraviolet–visible 600 μm core) connected to the upright optical microscope (Nikon Eclipse LV100). The illumination source of the microscope consists of a 50 W halogen lamp (Nikon LV-HL50W LL). The Rayleigh scattering from individual plasmonic nanostructures was collected using a ×50 objective (Nikon ×50 BD). The collected light was directed to the entrance slit (1,000 μm) of the spectrometer (Andor Shamrock SR303i) and dispersed onto a grating (150 lines mm^{-1}, blaze wavelength 800 nm), from which it was analysed by a thermoelectrically cooled charge-coupled device (CCD) camera (Andor Newton 920). Normalized scattering spectra I_{sc} from individual nanoantennas were obtained as a function of wavelength λ using the relation $I_{sc}(\lambda) = (S - D)/CRS$, where S is the collected signal from an area with nanoantenna, D is the signal from the nearby area without nanoantenna (dark signal for background correction), and CRS is the signal collected from the diffuse white certified reflectance standard (Labsphere SRS-99-020). CRS is used to correct the signal for the lamp spectrum. The acquisition time for each spectrum was 10 s. The obtained single-particle scattering spectra were fitted with a Lorentzian function (±50 nm from the peak position) to derive information about the temporal evolution of the peak position. As was previously shown[29,30,39], the changes in peak position are proportional to the hydrogen concentration in the indirectly probed Pd particle. For each data set (each particle size/shape) a new sample was used. Finally, we also notice that, owing to the low power of illumination used, light-induced heating of the sample is negligible[48], which allows reliable and quantitative analysis of both absorption and desorption isotherms, in contrast to the study by Baldi *et al.*[26], where electron-beam-induced heating effects render desorption isotherms unreliable.

SEM imaging and correlation with dark-field scattering spectroscopy.

To find nanostructures characterized in the SEM in the optical microscope for DFSS experiments, the following procedure was developed. First, with the aid of a scribing pen, the sample was marked with a line marker that was clearly visible in the optical microscope. Then, SEM imaging was done in a Zeiss Supra 60 VP (IXRF EDX) at 8 kV acceleration voltage nearby the markers at about 200–300 μm distance to avoid stray light from the marker interfering with the plasmonic nanoparticle measured in the experiment. When a suitable nanostructure was found, it was imaged at high magnification to resolve the structural details and estimate the size of the particle. Then, the said structure was imaged at several decreasingly lower magnifications to create a ‘map’ of the sample topography that would step-by-step allow the particle of interest to be found in the optical microscope used for DFSS.

FDTD simulations.

FDTD simulations were carried out using the commercial software FDTD Solutions (Lumerical). The simulation scheme is schematically depicted in Fig. 2e. On a semi-infinite (for practical purposes) silicon substrate we place a 50 nm layer of SiO_2 (refractive index 1.45), on top of which we place a gold nanosphere 100 nm in diameter with the adjacent Pd nanoparticle arranged in different configurations. The permittivity data are taken for Si from ref. 49, for Au from ref. 50 and for Pd/PdH_x from ref. 10. The mesh around the gold nanosphere is 1 nm; also, to resolve the swelling of Pd on H sorption, we use a 0.2 nm mesh. Normally incident, linearly polarized light is introduced via total-field/scattered-field conditions (inner red box in Fig. 2e), the scattered signal is measured as the flux of the Poynting vector in the scattered-field region (outer black box in Fig. 2e). The simulation volume is terminated by absorbing boundary conditions.

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Contributions

S.S. and C.L. planned the experiments, analysed the data, and wrote the paper. S.S. performed the single-particle measurements. C.W. and F.A.A.N. executed the ensemble measurements and XPS analysis. T.A.G., Y.A.D.F., G.N., F.W. and K.M.-P. synthesized and self-assembled the nanoparticle heterodimers. T.J.A. and D.Ś. performed the FDTD simulations. V.P.Z. contributed the theoretical analysis of lattice strain and dislocation formation. C.L. conceived the general approach and coordinated the project.

Competing interests

The authors declare no competing financial interests.

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Supplementary information

PDF files

1. 1.

Supplementary Information
Supplementary Information